Structure investigation of metastudtite, $UO_4 \cdot 2H_2O$

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The minerals studtite ($UO_4 \cdot 4H_2O$) and metastudtite ($UO_4 \cdot 2H_2O$) are the only natural occurring peroxide minerals. Studtite plays a potentially important role in a deep geologic repository for nuclear waste, especially if the direct disposal of spent nuclear fuel (SNF) is regarded [1]. While the structure of studtite is known [2], only a first principles model exists for metastudtite [3] and the phase relation is not fully understood. We synthesized studtite and metastudtite and investigated the dehydration process with x-ray diffraction. When applying the structure model [3] in spacegroup 62 (*P* nma) for metastudtite, a = 8.412(2) *Å*, b = 6.496(1) *Å* and c = 8.763(2) *Å* with R_{wp}= 5.89 % and R_p= 4.63 % are obtained from the Rietveld refinement. The bounding properties of water were studied with inelastic incoherent neutron scattering (IINS). The libration edge (LE) of water is present in studtite, proving existence of crystal water. This characteristic feature is missing in the metastudtite spectra, hence water in this structure is not free but has to be strongly bound to the UO_6-octahedra. From our findings we can conclude that the calculated structure by Weck et al.[3] for metastudtite is highly reasonable and *P* nma is the correct spacegroup to be assigned. Preliminary results from our synchrotron experiments also acknowledge this.

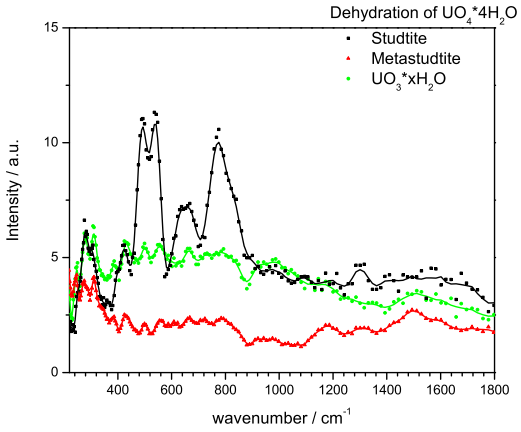

Figure 1: IINS spectra of studtit, metastudtite and the amorphous product after sintering at T = 250 °C. The LE is clearly visible in the studtite spectra.

[1] B. Hanson et al. Corrosion of commercial spent nuclear fuel. 1. Formation of studtite and metastudtite, Radiochim. Acta (93) 159-168, 2005.
[2] P.C. Burns and K.-A. Hughes Studtite, $[(UO_2)(O_2)(H_2O)_2](H_2O)_2$: The first structure of a peroxide mineral Amer.Min., 88, 1165-1168, 2003.
[3] P.F. Weck et al. Structures of uranyl peroxide hydrates: a first-principles study of studtite and metastudtite, Dalton Trans., 41, 9748, 2012.